

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 17-09-2007		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 1-Oct-2006 - 30-Jun-2007	
4. TITLE AND SUBTITLE ZnO Nanoelectronics			5a. CONTRACT NUMBER W911NF-06-1-0511		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS Olufemi Olowolafe, Robert L. Opila			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Delaware Ofc Vice Provost for Research University of Delaware Newark, DE 19716 -				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 51075-MS-II.1	
12. DISTRIBUTION AVAILABILITY STATEMENT Distribution authorized to U.S. Government Agencies Only, Contains Proprietary information					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We have demonstrated the aqueous growth of ZnO nanorods on a wide variety of substrates including Au, Al, Si, Pt, Ag, ITO, and silica. The rate of nucleation and the form of the crystals depends slightly upon the substrate. Additives can dramatically change the growth habit. The nanorods grow in the (1000) direction and are 0.1 – 10 µm long. Short, squat rods are appropriate as MEMS actuators, and we are acquiring a nanoindenter to characterize their piezo-electric properties. Long, thin rods may be used as photovoltaic antennae, sensors, or field-effect transistors. We are in the process of testing the conductivity of these crystals by placing the crystal across a metallization pattern and contacting it. The metallization pattern					
15. SUBJECT TERMS ZnO, nanostructures, electrical characterization,					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Olufemi Olowolafe
a. REPORT S	b. ABSTRACT U	c. THIS PAGE U			19b. TELEPHONE NUMBER 302-831-4272

## Report Title

Nanoscopic ZnO: Growth, Doping and Characterization

### ABSTRACT

We have demonstrated the aqueous growth of ZnO nanorods on a wide variety of substrates including Au, Al, Si, Pt, Ag, ITO, and silica. The rate of nucleation and the form of the crystals depends slightly upon the substrate. Additives can dramatically change the growth habit. The nanorods grow in the (1000) direction and are 0.1 – 10  $\mu$ m long. Short, squat rods are appropriate as MEMS actuators, and we are acquiring a nanoindenter to characterize their piezo-electric properties. Long, thin rods may be used as photovoltaic antennae, sensors, or field-effect transistors. We are in the process of testing the conductivity of these crystals by placing the crystal across a metallization pattern and contacting it. The metallization pattern provides the capability of making four-point contact. The integrity is ensured by deposition of Pt using a focused ion beam. The surface of the ZnO will be passivated with Si<sub>3</sub>N<sub>4</sub> and SiO<sub>2</sub>.

---

**List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

Number of Papers published in peer-reviewed journals: 0.00

---

**(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)**

Number of Papers published in non peer-reviewed journals: 0.00

---

**(c) Presentations**

Number of Presentations: 0.00

---

**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

---

**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

---

**(d) Manuscripts**

Number of Manuscripts:

---

Number of Inventions:

---

Graduate Students

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

#### **Names of Post Doctorates**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

#### **Names of Faculty Supported**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

#### **Names of Under Graduate students supported**

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

#### **Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....

The number of undergraduates funded by this agreement who graduated during this period with a degree in  
science, mathematics, engineering, or technology fields:.....

The number of undergraduates funded by your agreement who graduated during this period and will continue  
to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for  
Education, Research and Engineering:.....

The number of undergraduates funded by your agreement who graduated during this period and intend to  
work for the Department of Defense .....

The number of undergraduates funded by your agreement who graduated during this period and will receive  
scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....

#### **Names of Personnel receiving masters degrees**

NAME

**Total Number:**

#### **Names of personnel receiving PHDs**

NAME

**Total Number:**

**Names of other research staff**

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

**Sub Contractors (DD882)**

**Inventions (DD882)**

## Final Report

Nanoscopic ZnO: Growth, Doping and Characterization

by

Olufemi Olowolafe, Associate Professor,  
Department of Electrical and Computer Engineering,  
University of Delaware, Newark, DE 19716.  
Tel: (302) 831-4272; Fax: (302)831-4316  
olowolaf@ee.udel.edu

Robert L. Opila, Professor,  
Department of Materials and Engineering,  
University of Delaware, Newark, DE 19716.  
Tel: (302) 831-3128; Fax: (302)831-4545  
opila@udel.edu

A Final Report presented to

US Army Research Office,  
Attention: Dr. William V. Lampert,  
P.O. Box 12211,  
Research Triangle Park,  
North Carolina 27709-2211.

Zinc oxide (ZnO) has extraordinary properties as a wide band gap semiconductor, a transparent conductor, a piezoelectric material, and even a magnetic semiconductor. These unique material properties have attracted tremendous interest for various applications, including transparent UV light emitters [1], solar cell applications [2, 3] and, because of its large piezoelectric constant [4], a potential candidate as a micro-electromechanical (MEMS or NEMS) material [5], or in spintronics [6]. As such *ZnO will enhance current military needs such as photovoltaics, radiation-hard and high temperature electronics, and guidance. In addition ZnO will provide opportunity for future military applications such as spintronics.*

Tremendous attention has recently been paid to ZnO nanowires because of novel physical properties and their potential applications in fabricating nanoscale electronic and optoelectronic devices [7]. Recently, Huang et al. demonstrated a UV nanolaser at room temperature using highly-oriented ZnO nanowire arrays [8]. As synthesized, ZnO generally reveals n-type conduction with a typical carrier concentration of  $\sim 10^{17}/\text{cm}^3$ , which is smaller than the carrier concentration of  $\sim 10^{18}$  to  $10^{20}/\text{cm}^3$  required in a number of applications including laser diode applications. The control of carrier concentration remains a significant challenge. Properly-doped ZnO nanowires will have potential for diverse applications, including microelectronics/nanoelectronics, chemical and biological sensors and diagnosis, energy conversion and storage, light-emitting displays, catalysis, optical storage and drug delivery.

## Technical Approach

### 1. Synthesis of Nanostructures

The first device that we have grown includes an array of ZnO nanopillars on metals. Using wet chemical techniques, we have successfully grown clusters of nanopillars on Au, Al, Ti, Si, Pt, and Ag and are currently investigating other substrates including indium tin oxide (see Figure 1 below). The surfaces of the Al, Ti, and Si are presumably oxidized. The wet depositions were carried out using an aqueous equimolar solution of zinc nitrate and hexamethylenetetramine. The nanopillars grow with a (0001) texture as evidenced by their hexagonal structure and their x-ray diffraction pattern.

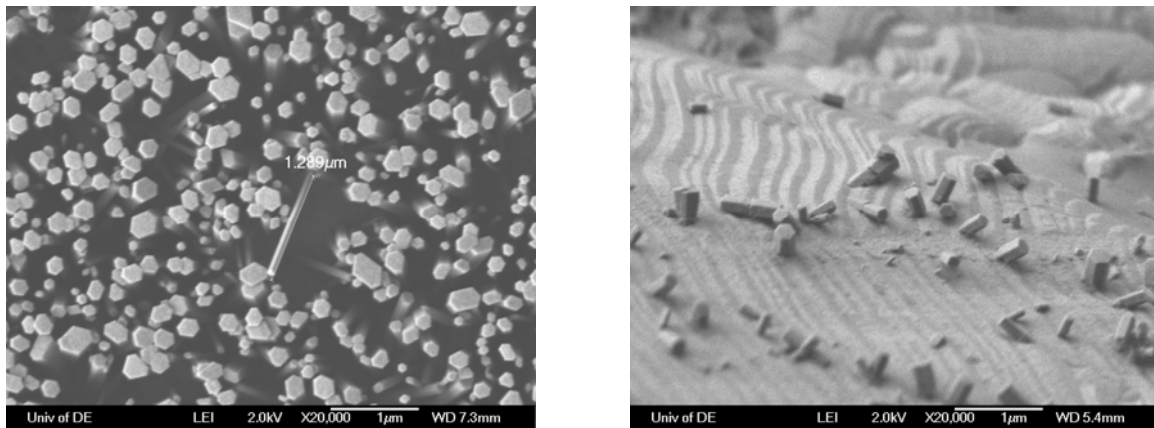


Figure 1. (a) Long, hexagonal structures grown on Ag. (b) Oriented (0001) textured nanorods grown on Pt substrates.

## 2. Electrical Characterization of ZnO Nanorods

We have begun to electrically characterize the conductivity of the nanorods. Our procedure is described below. We expect to be complete in one month (end of September 2007).

1. Grow long ZnO ( $> 10\text{ }\mu\text{m}$ ) nanorods (complete).
2. Design test pattern (shown below), which permits four-point probe of conductivity. We have included redundancy in the mask (there are 6 legs, where four is the minimum required). Mask done and test structure completed.
3. Align the nanorods with the test pattern. The movement is performed using a micromanipulator at the NSF National Nanotechnology Infrastructure Network at Penn State University (in progress).
4. Nanorods will be secured and electrical contact will be additionally ensured by depositing metal contact lines with a focused ion beam (FIB). We have made our first attempts to make electrical contact to one ZnO nanostructure used an FEI Dual Beam FIB. This instrument has a high spatial resolution, liquid metal, ion source, permitting us to measure the electrical properties (initially using a two point measurement). Here we etched small holes, approximately 100 nm, through the  $\text{SiO}_2$  layer, using a Ga ion beam. Once the holes were etched, lines were connected to the holes using the interaction of the ion beam with the deposited metal organic Pt compound (in progress).
5. Coat rods with  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  to minimize effects of surface conductivity. The passivations will be deposited using PECVD facility at NNIN PSU. (scheduled)
6. Electrical contact will be made by etching small contact holes through the passivation with  $\text{H}_3\text{PO}_4$  and HF to the ZnO. This will permit us to make electrical contact to the pads using the micrometer scale electrical tester at the NNIN facility at Penn State.

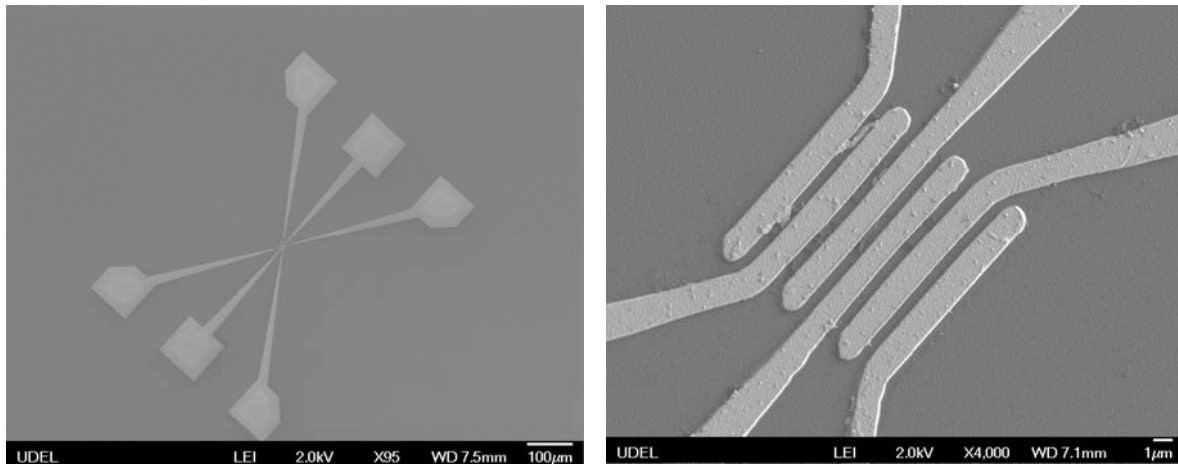


Figure 2. The test pattern to be used for four-point probe of nanorod conductivity.

## 3. Future work.

1. Doping of nanorods with electrically active  $p$  or  $n$  dopants.
2. Doping of nanorods with magnetic dopants for spintronics.

3. Test field effect of conductivity ZnO nanorods.
4. Test piezoelectric effect of ZnO nanorods using Nanoindenter that is being acquired through DURIP for use as MEMS actuator.
5. Test effects of ambient on surface conductivity of ZnO for use as sensor.
6. Develop structure to test photovoltaic effect of ZnO, and develop array of antennae for tuned PV.

## References

1. Look, D.C, Materials Science and Engineering, 2001. **B 80**: p. 383-387.
2. Nuruddin, A. and J.R. Abelson, Thin Solid Films, 2001. **394-63**: p. 49.
3. Lee, J.C., K.H. Kang, S.K. Kim, K.H. Yoon, I.J. Park and J. Song, Solar Energy Materials and Solar Cells, 2000. **64**: p. 185-195.
4. Noel, Y., C.M. Zicovich-Wilson, B. Civalieri, P. D'Arco and R. Dovesi, Phys. Rev. B, 2002. **65**: p. 014111-1 - 014111-9.
5. Martin, P.M., M.S. Good, J.W. Johnston, G.J. Posansky, L.J.B. Bond and S.L. Crawford, Thin Solid Films, 2000. **379**: p. 253-258.
6. Lawes, G., A.S. Risbud, A.P. Ramirez and R. Seshradri, Phys. Rev. B, 2005. **71**: p. 045201-1 - 045201-5.
7. C. Bower, W. Zhu, S. Jin, and O. Zhu, Appl. Phys. Lett. **77**, (2000) 830.
8. M. H. Huang, S. Mao, H. Feik, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science **292**, (2001) 1897.
9. Hsu, J.W.P., Z.R. Tian, N.C. Simmons, C.M. Matzke, J.A. Voigt and J. Liu, *Directed Spatial Organization of Zinc Oxide Nanorods*. Nanoletters, 2005. **5**: p. 83-86.
10. Yu, W.H., G.T. Fei, X.M. Chen, F.H. Xue and X.J. Xu, *Influence of defects on the ordering degree of nanopores made from anodic aluminum oxide*. Physics Letters A, 2006. **350**: p. 392-395.
11. Lin, Z.Q., D.H. Kim, X.D. Wu, L. Boosaheda, D. Stone, L. LaRose and T.P. Russell, *A rapid route to arrays of nanostructures in thin films*. Adv. Mater., 2002. **14**: p. 1373-1376.